Origin of the efficient light emission from inversion domain boundaries in GaN

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Intentionally-produced inversion domain boundaries in GaN have been reported to be highly efficient shallow recombination centers. Here I report a rationale for this phenomenon based on ab initio density-functional calculations. I also propose a model, based on the existence of polarization in GaN, of the observation that a domain boundary acts as a rectifying junction under voltage applied between the two opposite-polarity surfaces.

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Nitride semiconductors, and GaN in particular, are major competitors in the optoelectronics market at the high frequency end of the visible spectrum. Understandably, considerable attention has been devoted to the nature of recombination centers in In-alloyed GaN, both non-radiative (mainly threading dislocations) and radiative (allegedly, In-rich regions). Not nearly as much work exists on recombination centers in plain GaN. In recent times, extended defects originating from the formation of polarity domain boundaries, and known as inversion domain boundaries (henceforth IDB for brevity), have come into focus in this context. They have been studied theoretically [1], directly imaged by high-resolution TEM [2] and piezoresponse force microscopy [3], and finally, intentionally produced in MBE epitaxial growth on patterned substrates [4]. By means of integrated PL topography [4] it was observed that, unexpectedly, these IDBs exhibit a tenfold more intense light emission compared to plain Ga-face surface areas. The transition energy is about 30 meV below the normal emission, and unlike the latter, it is polarized in the plane of the defect. The IDBs thus qualify as highly efficient recombination centers. The first purpose of this paper is to report a rationale for this phenomenon, based on ab initio density-functional calculations. A further puzzling observation [5] is that an IDB between metal contacts placed on the Ga-face and N-face surface regions, acts as a rectifying junction (direct bias being Ga-face to N-face). Here, I also propose a model of the latter behavior, based on the existence of permanent bulk polarization in GaN [6].

Being a wurtzite crystal, GaN possesses a singular polar axis labeled (0001) with the convention that the positive direction points from the cation to the anion, and an attendant permanent polarization vector oriented as (000$\bar{1}$). There exist two geometrically distinct crystal terminations, the (0001) or Ga-face and (000$\bar{1}$) or N-face, whereby a Ga (respectively, a N) atom would have a single "dangling bond" orthogonal to the surface. Two regions of opposite polarity, conveniently labeled Ga-face and N-face, meet at an IDB. There are at least two plausible models thereof, which were discussed earlier by Northrup *et al.* [1]. In the first, cations and anions are exchanged in half of the crystal, giving rise to a geometrically undistorted interface, which however contains two (one N–N and one Ga–Ga) wrong bonds per cell [7]. The second model, also known as IDB* and found in Ref.1 to be decidedly favored energetically over the first, is obtained shifting one of the inverted half-cristals by half the cell length ($c/2$) along the singular axis. This enables all atoms to be correctly bonded, at the only cost of a modest distortion of the local bond angles, the largest single angle change being ∼109° to 90°. In this work, I will be considering the latter model.

I calculate total energies, forces, stress, and electronic potential and density from first-principles, within density functional theory [8] in the Ceperley-Alder [9] local-density approximation to exchange and correlation, using the accurate all-electron frozen-core Projector-Augmented Waves (PAW) method [10] as implemented [11] in the Vienna Ab-initio Simulation Package (VASP) [12]. The plane wave cutoff is set at 290 eV. The partial wave expansions for N and Ga include angular momenta up to $l=2$ and $l=3$, respectively, with all on-site projectors included. Ga $3d$ electrons are treated as valence. Accurate reciprocal-lattice grids are used, with no wrap-around aliasing allowed in Fourier transforms. Monkhorst-Pack k-space integration grids are used; for the bulk, converged results are obtained with the ($4\times4\times4$) mesh, tested up to the ($12\times12\times12$). The resulting crystal structure of GaN is a_{GaN}=3.160 Å, c/a_{GaN} =1.626, u=0.3769, which matches closely (maximum deviation: 0.9 % for a_{GaN}) the accepted experimental values a_{exp}=3.189 Å, c/a_{exp}=1.626, u=0.377 [13] – one of the best descriptions of bulk structure ever achieved for GaN.

The IDB* planar defect can be simulated in periodic boundary conditions via repeated supercells. I use a crystalline GaN orthorombic supercell comprised of 24 formula units (48 atoms), with linear dimensions (1, 1.626, 6 $\sqrt{3}$) in units of a_{GaN}. After testing the ($n\times1\times n$) and ($n\times2\times n$) k-point meshes with n=2,4, and 8, I used the ($4\times2\times4$) for all the results reported here. The symmetry of the system is found to be almost exactly D$_{2h}$, although this symmetry is not explicitly enforced. When it

is, the k-space grid includes 4 special points in the super-cell Brillouin reduced zone; otherwise the mesh comprises 8 points in the reduced zone.

Before relaxation, the formation energy of the IDB defect is 40 meV/Å². To allow for possible defect-induced strains, the cell length in the y direction (orthogonal to the defect plane) was adjusted, with the atomic geometries being constantly optimized to obtain residual force components below 0.01 eV/Å. The cell length does not change within numerical accuracy; some local relaxation occurs in the planes immediately adjacent the defect, all other atomic positions being unperturbed. Relaxation reduces the formation energy to 20 meV/Å², a rather small value compared to the 114 meV/Å² of two relaxed $(10\bar{1}0)$ surfaces of GaN [14], and agreeing well with the 25 meV/Å² of Ref.[1].

I calculate the transition energies, using the so called ΔSCF principle [18], as the combination of (variational) total energies of the system with varying number of electrons

$$E_{\mathrm{gap}} = E_{\mathrm{tot}}(N+1) - 2E_{\mathrm{tot}}(N) + E_{\mathrm{tot}}(N-1). \quad (1)$$

This expression is exact in the $N \to \infty$ limit, but it turns out to be pretty accurate also at finite N to estimate the gap of crystals [19]. The added charge is compensated by a uniform background. Since part of the excess charge localizes in the defect plane, I apply a correction $\sigma^2 d_{\mathrm{cell}}/2\varepsilon_r$ (σ the interface charge, d_{cell} the cell length, ε_r the static dielectric permittivity) to account for the spurious interaction of such sheet charges, screened by the static dielectric response of GaN. This correction is in the order of 10 μeV, i.e. fully negligible on the scale of other computational approximations (e.g. frozen core, LDA, etc.) and convergence errors.
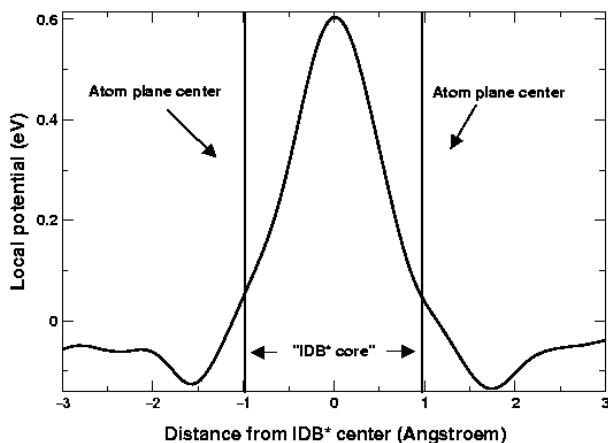

FIG. 1: Local self-consistent electronic potential at the IDB*

The transition energy obtained for the bulk undefected cell is 3.49 eV, in good agreement with experiment. For the defected cell, the transition energy is also 3.49 eV, thus predicting a red shift of zero, compared to the experimental value of 30 meV. In the calculations the excess electron or hole are added separately to the system, and they do not interact in any way, so that excitonic effect are not described.

However, in view of the low experimental temperature, it is fairly natural to suppose that the observed shift may be of excitonic origin. Although electron-hole interaction is not included, it is possible to pinpoint the origin of the effect looking at the precursors of the exciton, i.e. the electron and hole densities and attendant self-consistent potential. Specifically, let us examine in Fig. 1 the self-consistent electronic potential of the defected cell in the neutral charge state (no extra charge), filtered through a macroscopic average [16] eliminating the periodic microscopic oscillations. As can be seen, the potential in the vicinity of the defect is such as to attract electrons with its weak but far-reaching side wings on the outer side of the defect core, and repelling them off the core itself; contrarywise, holes are attracted to the defect core. Both electrons and holes are thus expected to localize in the vicinity of the defect (which should enhance excitonic interactions).
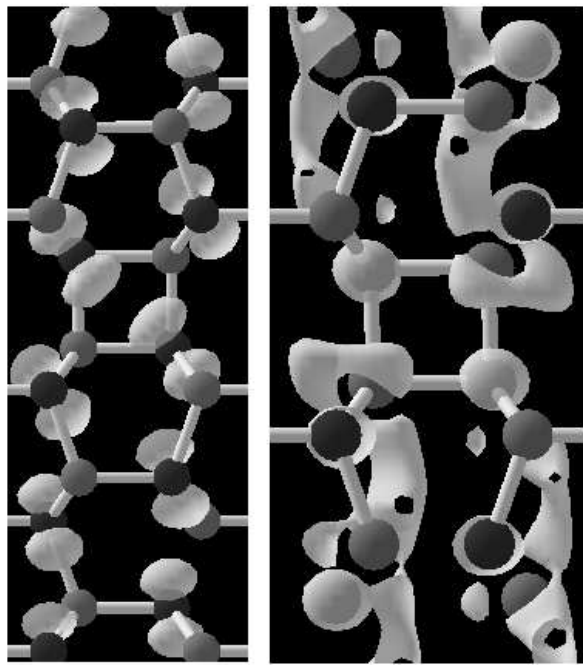

FIG. 2: Density of excess hole (left) and electron near the IDB* defect.

This is confirmed by inspection of the excess electron and hole charge densities, obtained as density differences between charged and neutral cells. As can be seen [17] in Fig. 2, electrons accumulate just outside the defect and onto the central repulsive wall, whereas (although this is not especially clear from the picture) the hole density is

enhanced in the defect core.

Inspection also helps rationalize the observed emission polarization in the defect plane. The electron density, mostly of cation s character, is "planarized" within the two-dimensional lateral wells of the defect potential. The hole density away from the defect consists of a lobe along the y direction: this is because the valence top state in GaN is a Γ_9 doublet of $p_x p_y$ nature (the x lobe is not visible, as the x direction is orthogonal to the plane of the picture); near the defect the p_y lobe pivots around the x axis admixing some character of the p_z singlet Γ_6 which lies some 50 meV lower than Γ_9 in unperturbed GaN. Overall this results in an enhanced directional overlap of the electron and hole functions.

A rationale for this admixture can be extracted from the following model (refer to Fig. 3). Consider zincblende
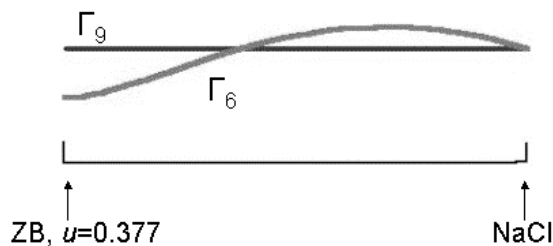

FIG. 3: Schematic of valence states admixture between wurtzite-like and NaCl-like environments.

GaN, with its three-fold degenerate valence band top. Stretch a bond along one of the (111)-equivalent direction; the degeneracy is removed, and as in wurtzite the Γ_6 singlet is lower than the Γ_9 doublet. Now displace, say, the anion along the chosen (111) direction, and monitor the relative position of the states. What is observed is the situation schematized in Fig. 3: as the distortion progresses the p_z singlet nears the doublet, becomes higher in energy (i.e. the band top), then merges back with the doublet into the threefold-degenerate valence top of the NaCl structure. The IDB* embodies indeed a local NaCl-like geometry, with one of the a-plane bonds at right angles with the polar-axis bond. This distortion is the cause of the admixture of the two top valence states.
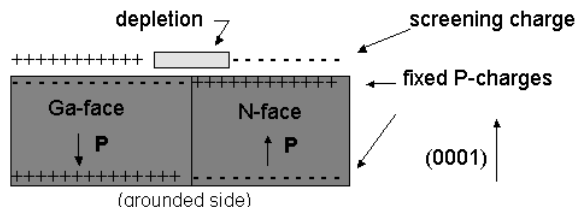

FIG. 4: Schematic of the polarization-driven rectifying mechanism.

Another remarkable effect, observed by Stutzmann *et al.* [5], is that an IDB* acts as a rectifying junction when electrically biased by two contacts placed respectively on the adjacent Ga- and N-face regions, direct-bias being realized by the positive pole on the Ga-face region. This behavior can be qualitatively explained by the existence of an intrinsic macroscopic polarization in wurtzite [6], as schematized in Fig. 4. The two adjacent opposite-polarity regions possess opposite intrinsic polarization vectors. This results in fixed polarization charges at the upper and lower ends of the sample, and changing sign across the IDB junction. On the upper side, mobile charges or impurities from the vacuum neutralize the polarization charges on each of the regions. At the border between the latter, the compensating charges will mutually neutralize and deplete, creating a junction-like potential which opposes the current flow from Ga-face to N-face. Direct polarization with the positive pole on the Ga-face side will then cause a current flow from Ga-face to N-face. It is difficult to say whether this current will flow subsurface or otherwise. Certainly, however, the lower side of the polarized layer, a few μm below the surface, will not be involved. Thereby, charges from, or defects in the nucleation layer are assumed to neutralize permanently the polarization charge.

In summary I have given an interpretation of the observed enhanced light emission from inversion domain boundaries in GaN, and I have suggested a qualitative explanation of the rectification effect observed across the boundaries themselves.

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